Department of

MATERIALS SCIENCE AND ENGINEERING

Doctoral Written Exam

Day 2

Core Areas covered:

ADVANCED THERMODYNAMICS OF MATERIALS
KINETICS ND PHASE TRANSFORMATIONS
STRUCTURE OF MATERIALS

Friday, January 27, 2006

Department of Materials Science and Engineering

DOCTORAL WRITTEN EXAM – Day 2
January 27, 2006

Your exam packet for day 2 contains a total of nine (9) questions from three (3) core areas, ADVANCED THERMODYNAMICS OF MATERIALS, KINETICS ND PHASE TRANSFORMATIONS, STRUCTURE OF MATERIALS, plus 20 answer sheets. Each question is on a separate page. A copy of the Table of Constants is included for your reference. **<u>You must submit 2 questions from each core area for grading</u>**. You will have 6 hours to complete the questions. You can obtain extra answer sheets from the proctor, if needed. Please use the following procedure:

Write a four (4) digit code of your choice, and your name on the 3 X 5 card provided. Use this code in place of your name to identify <u>all</u> answer sheets you submit for both days of the exam. Renee will keep the code information, sealed in an envelope, until after the exams are graded.

For each answer, use the question sheet as the first page of your answer. If additional pages are required, use the blank answer sheets provided. At the end of the examination, staple each question sheet and corresponding answer sheets for each question separately, put this instruction sheet on top of the questions you are turning in, and place them in one side of your exam folder. Place <u>all</u> other exam pages in the other side of your folder, and return <u>everything</u> to the proctor, or Renee if you finish before 2:30 P.M.

<u>Please be sure to complete the information required on each page</u>.

GOOD LUCK!

CODE NUMBER ________________

<u>CHECK THE 6 QUESTIONS YOU WISH TO HAVE GRADED:</u>

Advanced Thermodynamics <u>Of Materials</u>	Kinetics and Phase <u>Transformations</u>	<u>Structure of Materials</u>
1.______	4.______	7.______
2.______	5.______	8.______
3.______	6.______	9.______

Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS   CODE #________

1.

1 kg of steam at a pressure of one atmosphere is supercooled to 80^o C by being brought into contact with a reservoir at that temperature. While the steam does not condense immediately when it reaches 80^o C, it does after a couple of hours.

a) Calculate the total amount of heat exchanged between the water and the environment starting from the point that the steam was supercooled to 80^o C.

b) What is the entropy change of the water during the same period?

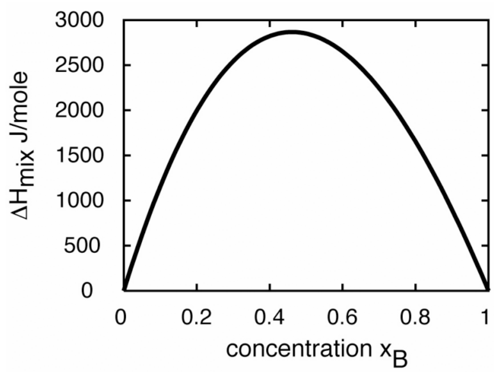
c) By how much does the entropy of the universe increase?

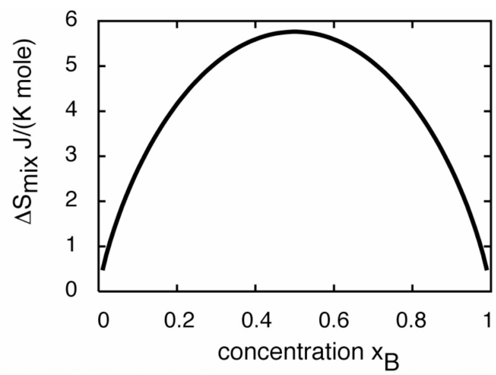
(Latent heat of vaporization is 2257 kJ/kg, average heat capacity of water is 4.2 kJ/kg·K and the heat capacity of steam is approximately 2.0 kJ/kg·K, boiling point of water is 100^o C). Use graphical depictions if you think that will help explain your reasoning.

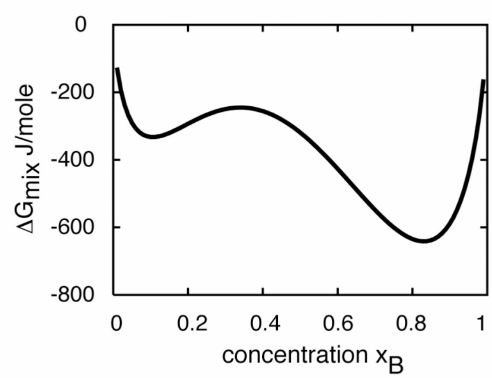
Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS CODE #________

2.

The mixing enthalpy, entropy and Gibbs free energy at 1 atm and 550 K for a mixture of *A* and *B* atoms are illustrated below.







Use the above plots to estimate a numerical value for $\mu_B - \mu_B^o$ and $\left(\frac{\partial(\mu_B - \mu_B^o)}{\partial T}\right)_{P,N_A,N_B}$ at x_B=0.8. Briefly describe how you estimated those values.

a) $\mu_B - \mu_B^o =$

b) $\left(\frac{\partial(\mu_B - \mu_B^o)}{\partial T}\right)_{P,N_A,N_B} =$

3.

a) Silver oxide becomes unstable above a certain temperature T_R, and spontaneously reduces to metallic silver and oxygen at a pressure of 1 atm. according to

$Ag_2O = 2\ Ag + ½\ O_2$ $\Delta G_R = 30540 - 66.11T$

Calculate T_R.

b) The combustion of carbon releases the heat of $\Delta H_C(298) = -393500$ J/mol, i.e.,
$C + O_2 = CO_2$ ΔH_C

Consider a process in which the combustion of carbon is used purely as a heat source. The enthalpy of combustion is used to heat the combustion products and silver oxide. At T_R silver oxide is reduced to silver, and the remaining components are further heated to 100 K above its melting temperature of 1234 K. The heat capacity of Ag_2O is given by $c_{p(Ag_2O)} = 67.1 + 0.0212T$, the enthalpy of fusion for silver is $\Delta H_{s/l} = 11090$ J/mol, and the enthalpy of reduction ΔH_R at T_R is 29240 J/mol. Other thermodynamic data needed can be found in the attached table.

Calculate the amount of carbon needed to produce 1 mol of liquid silver using this process.

Table A-2 The constant-pressure molar heat capacities of various substances ($c_p = a + bT + cT^{-2}$ J/mole·K)

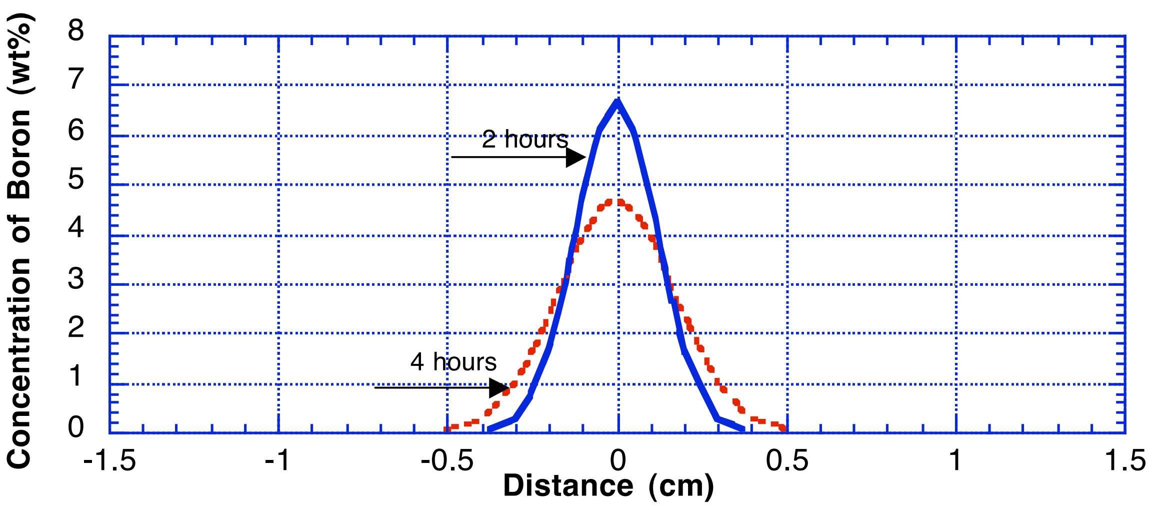
Substance	a	$b \times 10^3$	$c \times 10^{-5}$	Range, K	Remarks
Ag	21.30	8.54	1.51	298–1234 (T_m)	
$Ag_{(l)}$	30.50	—	—	1234–1600	
$Al_{(s)}$	20.67	12.38	—	298–937(T_m)	
$Al_{(l)}$	31.76	—	—	934–1600	
Al_2O_3	106.6	17.78	−28.53	298−2325(T_m)	
Ba(α)	−473.2	1587.0	128.2	298–648	
$Ba_{(\beta)}$	−5.69	80.33	—	648–1003	
BaO	53.30	4.35	−8.30	298–2286(T_m)	
$BaTiO_3$	121.46	8.54	−19.16	298–1800	
$C_{(graphite)}$	0.11	38.94	−1.48	298–1100	$-17.38\times10^{-6}T^2$
$C_{(graphite)}$	24.43	0.44	−31.63	1100–4000	
$C_{(diamond)}$	9.12	13.22	−6.19	298–1200	
CO	28.41	4.10	−0.46	298–2500	
CO_2	44.14	9.04	−8.54	298–2500	
$Ca_{(\alpha)}$	25.37	−7.26	—	298–716	$23.72 \times 10^{-6}T^2$
$Ca_{(\beta)}$	−0.36	41.25	—	716–1115	
CaO	49.62	4.51	−6.95	298–1177	
$CaTiO_3$	127.49	5.69	−27.99	298–1530	
$Cr_{(s)}$	24.43	9.87	−3.68	298–2130(T_m)	
Cr_2O_3	119.37	9.30	−15.65	298–1800	
$Cu_{(s)}$	22.64	6.28	—	298–1356(T_m)	
$Fe_{(\alpha/\delta)}$	37.12	6.17	—	298–1183/1664–1809	
$Fe_{(\gamma)}$	24.47	8.45	—	1187–1664	
$Fe_{(l)}$	41.8	—	—	1809–1873	
$H_2O_{(g)}$	30.00	10.71	0.33	298–2500	
$O_{2(g)}$	29.96	4.18	−1.67	298–3000	
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	626.34	91.21	−200.83	298–1738(T_m)	
N_2	27.87	4.27	—	298–2500	
Si_3N_4	70.54	98.74	—	298–900	
$SiO_{2(\alpha\text{-quartz})}$	43.89	1.00	−6.02	298–847	
Ti	22.09	10.46	—	298–1155	
$TiO_{2(rutile)}$	75.19	1.17	−18.20	298–1800	
$Zr_{(\alpha)}$	21.97	11.63	—	298–1136	
$Zr_{(\beta)}$	23.22	4.64	—	1136–2128	
$ZrO_{2(\alpha)}$	69.62	7.53	−14.06	298–1478	
$ZrO_{2(\beta)}$	74.48	—	—	1478–2950(T_m)	

4.

Due to the fact that boron suppresses the melting point of many metallic materials and also diffuses very rapidly in the solid state, boron-rich foils can be used for diffusion bonding. You are interested in investigating the bonding cycle that would be required to join two blocks of nickel with a 1mm thick foil of Ni-20wt%B. After 4 hours at 800˚C, the following boron profile shown below is measured. Assume the foil was centered at x=0.

a) From the information provided in the graph, determine the diffusivity of boron in nickel?

b) What is the length of a cycle at 800˚C that be required to ensure that there is no more than 0.5 wt% enrichment of boron at the original joint?



5.

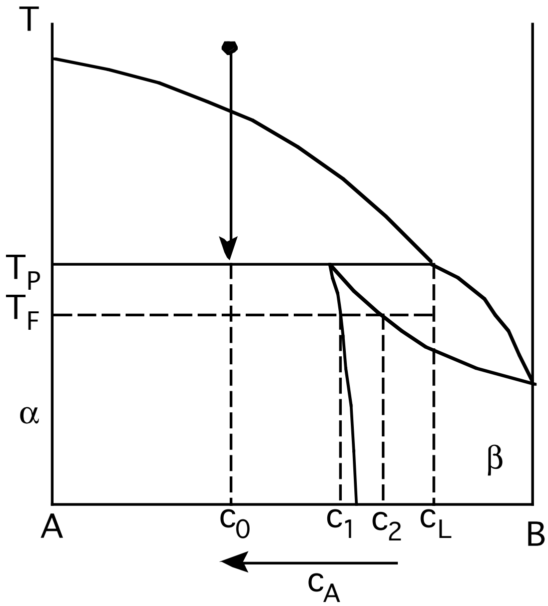
A Newtonian fluid is forced through two channels of same length and cross sectional areas but of different cross sections. One is circular with radius "R" and the other a channel of width "W" and thickness "t". Assume laminar flow, W>>t, ($W = 10 \times t$) and neglect end effects.

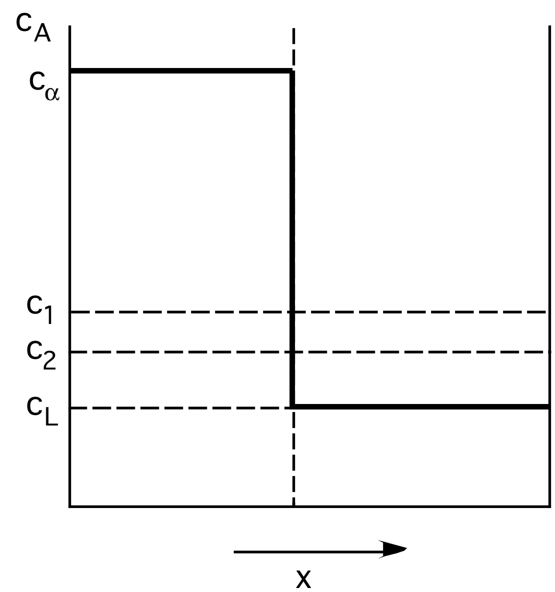
a) Under the same pressure gradient, how will the fluid flow rates differ between the tube and channel? (derive the difference in terms of W, t, and R)

b) What is the ratio of pressure gradients required to convey fluid at the same flow rate between tube and channel?

Day 2 – KINETICS AND PHASE TRANSFORMATIONS **CODE #________**

6.





Consider a peritectic reaction α + liq. = β, as illustrated in the above phase diagram. Assume that a melt of composition c_0 is quenched to a temperature just above the peritectic temperature, T_p, and held there until the equilibrium is reached. The phases present are α and liq., and their geometric arrangement is indicated in the adjacent schematic. Assume that the solid and liquid are perfectly separated, i.e., only one continuous and flat interface exists between them (simplest possible geometry). Now the temperature is dropped just below the peritectic temperature, say T_F. Obviously, phase β will now form.

a) How will this happen. Illustrate the process by sketching composition vs. length diagrams at different times. (Hint: Ask yourself which phases will appear, which will disappear, which interface will move. Which components will diffuse into, out of, or across which phases).

b) Assume some generic values for chemical diffusion coefficients in the liquid and solid of $6.2 \cdot 10^{-5}$ cm^2/s and $2.5 \cdot 10^{-9}$ cm^2/s respectively, and for the concentrations of species A the values are $c_\alpha = 0.22$, $c_0 = 0.14$, $c_1 = 0.11$, $c_2 = 0.085$, and $c_{liq.} = 0.05$ mol/cm^3. Establish a simple but justifiable model that allows you to calculate the amount of phase β that forms as a function of time. Ignore the time required for nucleation.

Day 2 – STRUCTURE OF MATERIALS **CODE #________**

7.

A tetragonal material has four atoms of the same kind per unit cell located at:

0 1/2 1/4; 1/2 0 1/4; 1/2 0 3/4; 0 1/2 3/4

a. Derive the simplified expressions for F^2.

b. What is the Bravais lattice of this crystal?

c. What are the values of F^2 for the 100, 002, 111, and 011 diffraction maxima?

8.

TiO_2 has a tetragonal crystal structure with a = 4.59 Å and c = 2.96 Å.

a) Is the [121] direction parallel to the normal of the (121) plane?

b) Along what direction does the (121) plane intersect the (110) surface?

c) What angle does this direction make with the [001] axis?

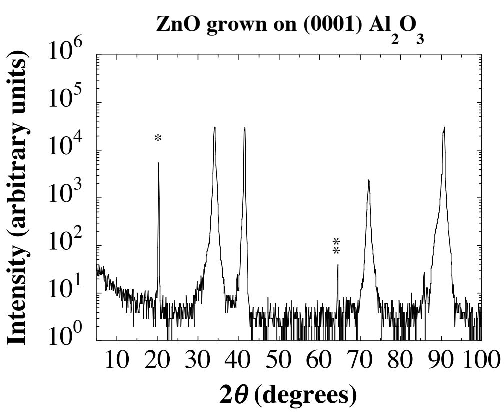
9.

An epitaxial ZnO thin film is grown on the (0001) surface of sapphire. Figure A shows the x-ray diffraction pattern (ϑ-2ϑ scan) of the sample. Figure B is the ϕ-scan of the sample film using the $10\bar{1}1$ reflection of ZnO. (i) Index all major peaks (except for the two peaks marked by * and **) appearing in Figure A. (ii) Find the orientation relationship between the ZnO film and the sapphire substrate.

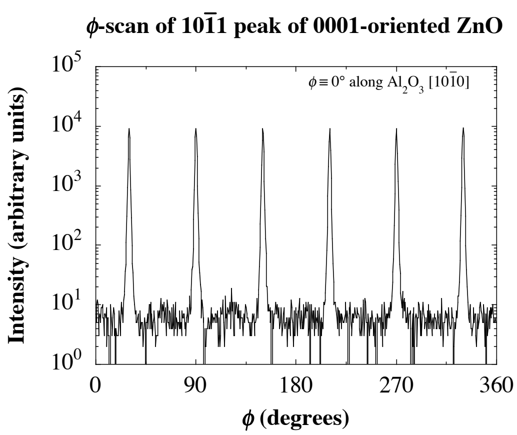
ZnO: hexagonal (*wurtzite*), a = 3.2495 Å, c = 5.2069 Å

Al_2O_3: hexagonal (*corundum*), a = 4.7628 Å, c=13.0032 Å

The wavelength of x-ray was 1.5406Å.



(A)



(B)